Cleavages of Silicon–Carbon Bonds in Tris(trimethylsilyl)methylsilicon Compounds by Trifluoroacetic Acid. Rearrangements and Anchimeric Assistance

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The fairly high rate of reaction of the highly sterically hindered compound $(Me_3Si)_3CSiMe_2Ph$ with CF_3CO_2H [to give $(Me_3Si)_3CSiMe_2O_2CCF_3$ and PhH] is consistent with the view that the rate-determining step involves the transfer of a proton from the acid to the *ipso*-carbon atom of the ring. The formation of the rearranged species $(Me_3Si)_2C(SiMe_2F)(SiMe_2O_2CCF_3)$ in the reaction of $(Me_3Si)_3$-CSiPhMeF with CF_3CO_2H suggests that the leaving of benzene from the initial protonated species generates a methyl-bridged silicon cation. Treatment of $(Me_3Si)_3CSiPhMeI$ with AgO_2CCF_3–CF_3CO_2H gives the rearranged $(Me_3Si)_2C(SiPhMe_2)(SiMe_2O_2CCF_3)$, which reacts with CF_3CO_2H under reflux to give $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$. In a remarkable example of anchimeric assistance by a γ-OMe group the compound $(Me_3Si)_3CSiMe_2OMe$ reacts readily with CF_3CO_2H at room temperature with evolution of methane, and formation finally of $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$, apparently *via* $(Me_3Si)_2C$-$(SiMe_2OMe)(SiMe_2O_2CCF_3)$. Sulphuric acid reacts very vigorously with $(Me_3Si)_3CSiMe_2OMe$, and hydrolysis of the initial product gives the diol $(Me_3Si)_3C(SiMe_2OH)_2$. This diol can also be obtained by hydrolysis of $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$.

Compounds containing the bulky tris(trimethylsilyl)methyl groups, $(Me_3Si)_3C$ (referred to as the 'trisyl' group, and often denoted below by the symbol Tsi) have been shown to display unusual chemical behaviour;[1-5] one of the most surprising features is the rearrangements which occur when compounds of the type $(Me_3Si)_3CSiR_2X$ react with appropriate electrophiles, such as silver salts AgY, to give products of the type $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$, apparently *via* a bridged cation of the type (1).[3,4] Equally unusual behaviour is observed also for related compounds of the type $(Me_3Si)_2C$-$(SiMe_2Z)(SiMe_2X)$, in which certain groups Z can provide very large anchimeric assistance to reactions at the Si–X bond.[5,6] We describe here some reactions of trisyl-silicon and related compounds which provide further illustrations of the types of behaviour mentioned; particular attention is paid to reactions with trifluoroacetic acid and with silver trifluoro-acetate, especially those involving cleavages of Si–C bonds.
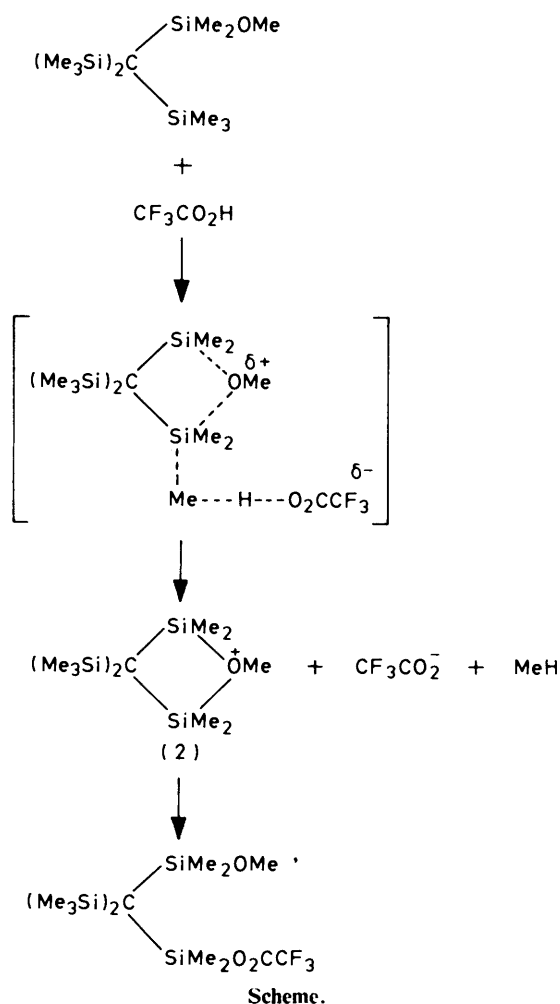
Results and Discussion

We initially examined reactions involving cleavage of Si–C bonds by trifluoroacetic acid. A preparative-scale reaction of TsiSiMe₂Ph with CF_3CO_2H was monitored by ¹H n.m.r. spectroscopy: all the signals from the aryl protons of the starting material disappeared and were replaced by a single resonance due to benzene, and work-up gave the expected TsiSiMe₂O₂CCF₃. The rate of the reaction was then measured at 37.5 °C by u.v. spectrophotometry, and the first-order rate constant was found to be 19 × 10^{-5} s⁻¹, 15 times as small as that (28 × 10^{-4} s⁻¹) observed for p-ClC₆H₄SiMe₃ under the same conditions. If we assume that the latter compound is *ca.* 5 times less reactive than PhSiMe₃, as it is in CH_3CO_2H–H_2SO_4,[7] then we can conclude that TsiSiMe₂Ph is roughly 75 times less readily cleaved than Me₃SiPh. This factor is small in relation to the very great inhibition by the trisyl group to nucleophilic attack at a silicon atom to which it is attached,[1] and the result is consistent with the view that the rate-determining step in cleavage of aryl–silicon bonds by acids is normally the attachment of a proton to the carbon atom of the aryl–Si bond.[8,9] The lower rate of cleavage of TsiSiMe₂Ph than of Me₃SiPh can reasonably be attributed to steric hindrance to (*a*) solvation of the (forming) protonated species, and (*b*) the geometry change at the *ipso* carbon.

(1)
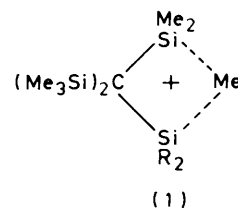
If this picture of the reaction is correct, then the separation of benzene from the initial protonated complex should leave a silicocation of type (1),[1,3,4] and so rearrangement would be expected. This could not (without isotopic labelling) be observed in the reaction of TsiSiMe₂Ph because the rearranged and unrearranged products would be identical, and so we turned to TsiSiMePhF. This compound reacted with CF_3CO_2H during 65 h under reflux to give almost exclusively the rearranged species $(Me_3Si)_2C(SiMe_2F)(SiMe_2O_2CCF_3)$. (The yield of this product isolated pure was not high, presumably because of reactions during work-up, but the ¹H n.m.r. spectrum of the crude product was identical, except for some very small additional peaks, with that of the purified material.) The markedly lower reactivity of TsiSiMePhF than of TsiSi-Me₂Ph towards the acid can be attributed to the inductive effect of the fluorine atom, which reduces the stabilization of the Wheland intermediate by the silyl group, and is consistent with observations in simpler systems.[9]

Treatment of TsiSiPhMeI with an equimolar amount of AgO_2CCF_3 in CF_3CO_2H at room temperature gave the rearranged species $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCF_3)$. (We expected this to be the major product, but, in the light of the results obtained in reactions of this iodide with other silver salts under other conditions[3] we were surprised that no detectable amount of the unrearranged product TsiSiPhMeO₂-CCF₃ was present.) The initial product was then refluxed with CF_3CO_2H for 7 h (though reaction may have been complete in a much shorter time), after which all the original ¹H n.m.r. signals from the aryl protons had disappeared and been replaced by a singlet due to benzene. Removal of the solvent gave $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$.

A similar reaction sequence was carried out starting from TsiSiPh₂I. The initial product from reaction with AgO_2CCF_3–

$(Me_3Si)_2C$ — SiMe$_2$OMe / SiMe$_3$

+

CF$_3$CO$_2$H

↓

$[(Me_3Si)_2C$ SiMe$_2$ / OMe δ+ / SiMe$_2$ / δ- Me --- H --- O$_2$CCF$_3]$

↓

$(Me_3Si)_2C$ SiMe$_2$ / $\overset{+}{O}$Me / SiMe$_2$ + CF$_3$CO$_2^-$ + MeH

(2)

↓

$(Me_3Si)_2C$ — SiMe$_2$OMe · / SiMe$_2$O$_2$CCF$_3$

Scheme.

CF$_3$CO$_2$H was the expected (Me$_3$Si)$_2$C(SiPh$_2$Me)(SiMe$_2$O$_2$-CCF$_3$). In the subsequent refluxing of this product with CF$_3$CO$_2$H all the original aryl proton peaks disappeared during 15 h and were replaced by a singlet due to benzene, but the δ 0.1—0.6 region of the spectrum showed a large number of peaks and thus the presence of several products, and these were not investigated. No reaction occurred when solutions of TsiSiCl$_3$ or TsiSiPhCl$_2$ in AgO$_2$CCF$_3$–CF$_3$CO$_2$H were refluxed for 24 h.

We next turned to the cleavage of Si–Me bonds. The compound (Me$_3$Si)$_4$C, as expected, underwent no reaction when refluxed with CF$_3$CO$_2$H for 3 h. In contrast, TsiSiMe$_2$-OMe reacted readily at room temperature, and work-up after 30 min gave (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$. When the reaction was carried out in an n.m.r. tube at 35 °C the ¹H n.m.r. spectrum showed that after 4 min ca. 25% of the TsiSiMe$_2$OMe was still present along with 30% of (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$, and a third component, accounting for the remaining 45%, gave signals consistent with its being (Me$_3$Si)$_2$C(SiMe$_2$OMe)-(SiMe$_2$O$_2$CCF$_3$). On further reaction both this and the starting material completely disappeared, leaving only (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$. No further reaction occurred during 5 h under gentle reflux.

This very ready cleavage of an Si–Me bond by CF$_3$CO$_2$H is remarkable. It can be attributed to the large anchimeric assistance by the γ-OMe group [and thus the stability of the bridged cation (2)], as depicted in the Scheme. [The ability of

the γ-OMe group to induce abnormally high reactivity in systems of the type under study was first suspected because of the result just described, and was confirmed more recently by observation of the very high reactivity of the compound (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiMe$_2$Cl) in methanolysis.⁵] The subsequent conversion of (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiMe$_2$O$_2$CCF$_3$) into (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$) presumably involves anchimeric assistance by the O$_2$CCF$_3$ group to leaving of the protonated methoxy group.

In view of the anchimeric assistance which can be provided by a γ-O$_2$CCF$_3$ group, we thought that (Me$_3$Si)$_2$C(SiMe$_2$O$_2$-CCF$_3$)$_2$ might undergo solvolysis fairly readily (cf. ref. 5). No reaction was observed in 1 h in refluxing MeOH, but complete conversion into the diol (Me$_3$Si)$_2$C(SiMe$_2$OH)$_2$ occurred upon treatment with (a) 1 : 1 MeOH–H$_2$O at 75 °C for 1 h or (b) 10% H$_2$O–Me$_2$CO under reflux for 8 h. (The mono-trifluoro-acetate TsiSiMe$_2$O$_2$CCF$_3$ is inert under these conditions.)

The diol was also made in another way. Since CF$_3$CO$_2$H reacted readily with TsiSiMe$_2$OMe, concentrated sulphuric acid, a much stronger acid, could be expected to react even more readily; indeed, a vigorous reaction, with gas evolution, occurred when the acid was added to TsiSiMe$_2$OMe in an n.m.r. tube. The ¹H spectrum taken as quickly as possible showed no signals from the starting material, but instead two new peaks in 2 : 3 ratio. (No further change occurred in 5 h.) An attempt to isolate the product from a larger scale reaction gave trouble because, it seemed, of hydrolysis during work-up; thus in another experiment, 5 min after mixing of the reagents the solution was added to ice–water; extraction with CH$_2$Cl$_2$ and removal of the solvent gave exclusively (Me$_3$Si)$_2$C-(SiMe$_2$OH)$_2$. (This procedure provides a good route to this diol.) It seems very likely that the initially observed product was (Me$_3$Si)$_2$C(SiMe$_2$OSO$_3$H)$_2$, formed via the very reactive (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiMe$_2$OSO$_3$H).

In view of the remarkable effects of the γ-OMe group, we decided to examine briefly some compounds containing the methoxy group at the functional centre. Thus TsiSiMe(OMe)I was treated with an excess of AgO$_2$CCF$_3$ in CF$_3$CO$_2$H for 15 min and the solution was filtered and evaporated to give a solid, which from its ¹H n.m.r. spectrum was mainly TsiSiMe-(OMe)(O$_2$CCF$_3$) along with ca. 10% of (Me$_3$Si)$_2$C(SiMe$_2$O$_2$-CCF$_3$)$_2$. Thus the presence of the α-OMe group greatly reduces the tendency to formation of rearranged product. No reaction occurred when the TsiSiMe(OMe)(O$_2$CCF$_3$) was refluxed with CF$_3$CO$_2$H for 1 h, indicating that anchimeric assistance by an OMe group to cleavage of a γ-Si–Me bond is greatly reduced by the presence of an α-O$_2$CCF$_3$ group.

Experimental

Reaction of TsiSiMe$_2$Ph *with* CF$_3$CO$_2$H.—(*a*) A solution of TsiSiMe$_2$Ph (1.0 g, 2.7 mmol) in CF$_3$CO$_2$H (10 cm^3) was refluxed for 6 h. [Reaction must have been complete in a much shorter time; see (*b*).] In the ^{1}H n.m.r. spectrum of the solution the original multiplet due to the aryl protons had been replaced by a singlet at δ 7.15 attributable to benzene. Addition of hexane (50 cm^3) followed by evaporation left a solid which on the basis of its ^{1}H n.m.r. spectrum [δ 0.31 (27 H, s, SiMe$_3$) and 0.64 (6 H, s, SiMe$_2$)] was judged to be TsiSiMe$_2$O$_2$CCF$_3$. A sample recrystallized from MeOH and sublimed at low pressure had the same ^{1}H n.m.r. spectrum, and this and the other physical properties were identical with those of an authentic sample.[3] The ^{19}F n.m.r. spectrum showed a singlet at −76.2 p.p.m., and the mass spectrum had the base peak at *m/z* 387 ([*M* − Me]$^+$) and other significant peaks at 309 (30%), 293 (20), 201 (50, [*M* − Me$_3$SiO$_2$CCF$_3$ − Me]$^+$), and 73 (80, [Me$_3$Si]$^+$).

(*b*) The rate of cleavage of TsiSiMe$_2$Ph in *ca.* 0.005M-solution in CF$_3$CO$_2$H (the organosilane was initially dissolved in a very small amount of CCl$_4$) at 37.5 ± 0.2 °C was determined by recording the change in the optical density at 272 nm (*cf.* ref. 13). Good first-order kinetics were observed and the value of the first-order rate constant (average of three runs) was 19 × 10^{-5} s^{-1}.

A similar procedure, also using a wavelength of 272 nm, gave a value of the first-order rate constant for *p*-ClC$_6$H$_4$-SiMe$_3$ of 28 × 10^{-4} s^{-1}.

Reaction of TsiSiPhMeF *with* CF$_3$CO$_2$H.—In a small-scale reaction monitored by ^{1}H n.m.r. spectroscopy, the original aryl proton multiplet was replaced by a singlet at δ 7.15 due to benzene during 65 h under reflux.

A solution of TsiSiPhMeF (1.0 g, 2.7 mmol) in CF$_3$CO$_2$H (10 cm^3) was refluxed for 65 h, then added to hexane (50 cm^3). Removal of the solvent left a solid which from its ^{1}H n.m.r. spectrum [δ 0.40 (18 H, s, Me$_3$Si), 0.55 (6 H, d, *J* 7.5 Hz, SiMe$_2$F), and 0.74 (6 H, s, SiMe$_2$O$_2$CCF$_3$)] was judged to be virtually pure (*fluorodimethylsilyl*)(*dimethyltrifluoroacetoxy-silyl*)*bis*(*trimethylsilyl*)*methane*. However, after recrystallization from MeOH followed by sublimation under reduced pressure, the recovered material (0.50 g, 45%) appeared to contain small amounts of impurities, and so it was subjected to preparative t.l.c. (SiO$_2$, hexane), which removed small amounts of two other compounds from the main product. The purified sample of the latter, m.p. 160 °C, ν(C=O) 1 765 cm^{-1}, gave the ^{1}H n.m.r. spectrum already noted; the ^{19}F n.m.r. spectrum showed peaks at −75.8 (3 F, s, CF$_3$) and −144.1 [1 F, septet, ^3J(FH) 7.5 Hz, SiMe$_2$F] (Found: C, 39.2, H, 7.8. C$_{13}$H$_{30}$F$_4$-O$_2$Si$_4$ requires C, 38.4; H, 7.4%).

Reaction of TsiSiPhMeI *and* (Me$_3$Si)$_2$C(SiPhMe$_2$)(SiMe$_2$-O$_2$CCF$_3$) *with* AgO$_2$CCF$_3$–CF$_3$CO$_2$H.—A solution of AgO$_2$-CCF$_3$ (0.24 mmol) was made by dissolving Ag$_2$CO$_3$ (0.033 g, 0.12 mmol) in CF$_3$CO$_2$H (3 cm^3) and TsiSiPhMeI (0.109 g, 0.23 mmol) was added. The mixture was stirred at room temperature for 30 min then filtered, and the filtrate was evaporated. A solution of the residual solid in CCl$_4$ (containing a little CH$_2$Cl$_2$) showed ^{1}H n.m.r. peaks at δ 0.29 (18 H, s, SiMe$_3$), 0.40 (6 H, s, SiPh*Me$_2$*), 0.61 (6 H, s, SiMe$_2$O$_2$CCF$_3$), and 7.2—7.8 (5 H, m, Ph), judged to be attributable to (Me$_3$Si)$_2$C(SiPhMe$_2$)(SiMe$_2$O$_2$CCF$_3$). The solid was recovered and its solution in CF$_3$CO$_2$H (3 cm^3) was refluxed for 7 h, after which the multiplet at δ 7.2—7.8 had been replaced by a singlet at δ 7.15 due to benzene. The solvent was removed under reduced pressure to leave a solid which had a ^{1}H n.m.r. spectrum identical with that of (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$. A sample (0.06 g, 52%) recrystallized from EtOH had physical constants identical with those of an authentic sample.

Reaction of TsiSiPh$_2$I *with* AgO$_2$CCF$_3$–CF$_3$COOH.—Silver carbonate (0.028 g, 0.10 mmol) was dissolved in CF$_3$-CO$_2$H (3 cm^3) and TsiSiPh$_2$I (0.10 g, 0.18 mmol) was added. The mixture was stirred at room temperature for 30 min then filtered, and the filtrate was added to hexane (20 cm^3). The solvents were removed under reduced pressure to leave a solid which, from its ^{1}H n.m.r. spectrum, was judged to be almost exclusively (*dimethyltrifluoroacetoxysilyl*)(*methyldi-phenylsilyl*)*bis*(*trimethylsilyl*)*methane*, δ 0.30 (18 H, s, SiMe$_3$), 0.46 (6 H, s, SiMe$_2$O$_2$CCF$_3$), 1.12 (3 H, s, SiPh$_2$*Me*), and 7.3—8.0 (10 H, m, Ph). A sample recrystallized from EtOH, m.p. 94 °C, ν(C=O) 1 765 cm^{-1}, gave the same ^{1}H n.m.r. spectrum and showed a singlet in its ^{19}F n.m.r. spectrum at −75.1 p.p.m. (Found: C, 54.4; H, 7.3. C$_{24}$H$_{37}$F$_3$O$_2$Si$_4$ requires C, 54.7; H, 7.1%). The base peak in the mass spectrum was at *m/z* 197 ([Ph$_2$MeSi]$^+$), and other significant peaks were at *m/z* 526 (1%, [*M*]$^+$), 511 (5, [*M* − Me]$^+$), 216 (55), 135 (60, [PhMe$_2$Si]$^+$), 105 (75), and 73 (20, [Me$_3$Si]$^+$).

Reaction of (Me$_3$Si)$_2$C(SiPh$_2$Me)(SiMe$_2$O$_2$CCF$_3$) *with* CF$_3$CO$_2$H.—The reaction just described was repeated, but after the removal of the AgI the filtrate was refluxed for 15 h. After this time the original multiplet due to the aryl protons had been replaced by a singlet due to benzene. There were numerous peaks in the δ 0.1—0.6 region, and the products were not investigated.

Reaction of TsiSiMe$_2$OMe *with* CF$_3$CO$_2$H.—(*a*) When TsiSiMe$_2$OMe was dissolved in CF$_3$CO$_2$H in an n.m.r. tube (at 35 °C), the ^{1}H n.m.r. spectrum, in addition to singlets at δ 0.45 and 0.83 in 9 : 2 ratio due to TsiSiMe$_2$OMe, showed singlets at δ 0.42 and 0.78 in 3 : 2 ratio attributable to (Me$_3$Si)$_2$-C(SiMe$_2$O$_2$CCF$_3$)$_2$ and further singlets at δ 0.40, 0.56, 0.76, and 3.58 in 6 : 2 : 2 : 1 ratio thought to be due to (Me$_3$Si)$_2$-C(SiMe$_2$OMe)(SiMe$_2$O$_2$CCF$_3$). After 4 min these three compounds were present in *ca.* 25 : 45 : 30 ratio, this point being that at which the concentration of the (presumed) (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiMe$_2$O$_2$CCF$_3$) reached its maximum. After 30 min only (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$ was present. No further change occurred during 5 h under gentle reflux.

[It is noteworthy that the chemical shifts in CF$_3$CO$_2$H of these and other compounds studied were significantly different from those in CCl$_4$. Thus in the latter solvent TsiSiMe$_2$OMe shows resonances at δ 0.36 and 0.70, and (Me$_3$Si)$_2$C(SiMe$_2$O$_2$-CCF$_3$)$_2$ resonances at δ 0.32 and 0.65.]

(*b*) A solution of TsiSiMe$_2$OMe (0.14 g) in CF$_3$CO$_2$H (5 cm^3) was kept at room temperature for 30 min then added to hexane (25 cm^3). The solvents were evaporated off to leave (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$ (0.16 g, 74%), the properties of which were identical with those of an authentic sample (Found: C, 36.2; H, 6.2. Calc. for C$_{15}$H$_{30}$F$_6$O$_4$Si$_4$: C, 36.0; H, 6.0%).

Reaction of TsiSiMe(OMe)I *with* AgO$_2$CCF$_3$–CF$_3$CO$_2$H.—Silver carbonate (0.44 g) was dissolved in CF$_3$CO$_2$H (15 cm^3) and TsiSiMe(OMe)I (0.34 g) was added with stirring. After 15 min the solution was filtered to remove AgI, and the solvent was removed under reduced pressure to leave a solid, the ^{1}H n.m.r. spectrum of which indicated that it consisted mainly of TsiSiMe(OMe)(O$_2$CCF$_3$) [δ 0.27 (27 H, s, SiMe$_3$), 0.60 (3 H, s, SiMe), and 3.64 (3 H, s, OMe)] along with about 10% of (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CF$_3$)$_2$. Recrystallization from MeOH followed by sublimation under reduced pressure gave pure [*methoxy*(*methyl*)*trifluoroacetoxysilyl*]*tris*(*trimethylsilyl*)-*methane* (0.26 g, 79%), m.p. 207—210 °C (sealed tube), ν(C=O) 1 765 cm^{-1}, ^{1}H n.m.r. spectrum as just noted (Found: C, 40.2; H, 8.1. C$_{14}$H$_{33}$F$_3$O$_3$Si$_4$ requires C, 40.2; H, 7.9%).

Treatment of TsiSiCl₃ *and* TsiSiPhCl₂ *with* AgO₂CCF₃–CF₃CO₂H.—(*a*) Silver carbonate (20 mmol) was dissolved in CF₃CO₂H (10 cm³), TsiSiCl₃ (1.30 mmol) was added, and the solution was refluxed for 24 h. No change was observed in the ¹H n.m.r. spectrum.

(*b*) The same result was obtained from TsiSiPhCl₂ (5 mg), Ag₂CO₃ (0.033 g), and CF₃CO₂H (3 cm³).

Reaction of TsiSiMe₂OMe *with Sulphuric Acid.*—(*a*) Concentrated sulphuric acid (1 cm³) was added to a solution of TsiSiMe₂OMe (10 mg) in two drops (*ca.* 0.1 cm³) of CH₂Cl₂ in an n.m.r. tube. Vigorous gas evolution occurred, and the ¹H n.m.r. spectrum showed only two singlets, at δ *ca.* 0.95 and 0.57, in 2 : 3 ratio. No further change occurred during 5 h at room temperature.

(*b*) Concentrated sulphuric acid (1 cm³) was added to a solution of TsiSiMe₂OMe (20 mg) in two drops (*ca.* 0.1 cm³) of CH₂Cl₂. After 5 min the solution was added carefully to ice–water. Extraction with CH₂Cl₂, followed by separation, drying (MgSO₄), and evaporation of the extract gave a solid which had ¹H n.m.r. and mass spectra identical with those of an authentic sample of (Me₃Si)₂C(SiMe₂OH)₂ (see later).

Treatment of TsiSiMe(OMe)(O₂CCF₃) *with* CF₃CO₂H.—No reaction occurred, as indicated by the ¹H n.m.r. spectrum, when a solution of TsiSiMe(OMe)(O₂CCF₃) in CF₃CO₂H was refluxed for 1 h.

Solvolysis of (Me₃Si)₂C(SiMe₂O₂CCF₃)₂.—(*a*) No reaction occurred, as indicated by the ¹H n.m.r. spectrum, when a solution of (Me₂Si)₂C(SiMe₂O₂CCF₃)₂ in MeOH was refluxed for 1 h.

(*b*) A mixture of a small amount of (Me₃Si)₂C(SiMe₂O₂-CCF₃)₂ with 1 : 1 v/v H₂O–MeOH in an n.m.r. tube was kept at 75 °C for 1 h. After this time the solution showed only two singlets, in 3 : 2 ratio, at δ *ca.* 0.40 and 0.48, believed to be due to (Me₃Si)₂C(SiMe₂OH)₂.

(*c*) A solution of (Me₃Si)₂C(SiMe₂O₂CCF₃)₂ (0.95 g) in 10% v/v H₂O–Me₂CO (15 cm³) was refluxed for 8 h. After cooling, the solvent was evaporated off under reduced pressure. The residue [the ¹H n.m.r. spectrum of which indicated that it was almost exclusively (Me₃Si)₂C(SiMe₂OH)₂] was sublimed to give *bis(hydroxydimethylsilyl)bis(trimethylsilyl)methane* (0.31 g, 53%); ¹H n.m.r. spectrum δ 0.28 (18 H, s, SiMe₃), 0.34 (12 H, s, SiMe₂), and 2.15br (2 H, s, OH) (Found:

C, 43.0; H, 10.45. C₁₁H₃₂O₂Si₄ requires C, 42.8; H, 10.45%). In the mass spectrum the base peak was at *m/z* 275 ([*M* − H₂O − Me]⁺); there was no parent ion peak, and the peak at *m/z* 293 ([*M* − Me]⁺) had a relative intensity of only 5%. Other significant peaks were at *m/z* 292 (3%, [*M* − CH₄]⁺), 291 (8, [*M* − OH]⁺), 290 (7, [*M* − H₂O]⁺), 219 (11), 203 (20), 187 (35), 129 (25), and 73 (50, [Me₃Si]⁺).

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